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(54) [Title of the invention]

Heat Ray Shielding Resin Sheet Material and Liquid Additive For Use in Its Manufacture.

(57) [Summary]

[Topic] To offer a heat ray shielding material that retains excellent visible light transmittance, shows high heat ray shielding property and has excellent strength such as impact resistance, and that can be manufactured by a simple method without using complicated manufacturing method or expensive physical film formation method.

[Method for solution] The heat ray shielding resin sheet material that has maximum transmittance in the visible light region and minimum transmittance based on showing strong absorption in infrared region based on dispersing hexa boride fine particles such as LaB<sub>6</sub> taken as heat ray shielding component in polycarbonate resin or acrylic resin. ITO fine particles and / or ATO fine particles can also be dispersed along with hexa boride fine particles.

[Scope of patent claims]

[Claim 1] The heat ray shielding resin sheet material has the characteristic of dispersing hexa boride fine particles, or dispersing hexa boride fine particles and ITO fine particles and / or ATO fine particles taken as heat ray shielding component in a transparent resin base material.

[Claim 2] The heat ray shielding resin sheet material described above in claim number 1 in which the hexa boride mentioned above is at least 1 compound chosen from  $\text{LaB}_6$ ,  $\text{CeB}_6$ ,  $\text{PrB}_6$ ,  $\text{NdB}_6$ ,  $\text{GdB}_6$ ,  $\text{TbB}_6$ ,  $\text{DyB}_6$ ,  $\text{HoB}_6$ ,  $\text{YB}_6$ ,  $\text{SmB}_6$ ,  $\text{EuB}_6$ ,  $\text{ErB}_6$ ,  $\text{TmB}_6$ ,  $\text{YbB}_6$ ,  $\text{LuB}_6$ ,  $\text{SrB}_6$  and  $\text{CaB}_6$ .

[Claim 3] The heat ray shielding resin sheet material described above in claim number 1 or 2 in which the hexa boride fine particles, ITO fine particles and ATO fine particles have average particle diameter of less than 200 nm.

[Claim 4] The heat ray shielding resin sheet material described above in any one of the claim numbers from 1 ~ 3 in which the content of heat ray shielding component mentioned above is  $0.05 \sim 19 \text{ g per } 1 \text{ m}^2$  heat ray shielding resin sheet material.

[Claim 5] The heat ray shielding resin sheet material described above in any one of the claim numbers from 1 ~ 4 in which the proportion of hexa boride fine particles and ITO fine particles and / or ATO fine particles mentioned above is within the range from 0.1:99.9 ~ 90:10 in terms of weight ratio.

[Claim 6] The heat ray shielding resin sheet material described above in any one of the claim numbers from 1 ~ 5 in which the resin base material mentioned above is formed from polycarbonate resin or acrylic resin.

[Claim 7] The heat ray shielding resin sheet material has the characteristic of forming resin film containing ultraviolet rays absorption agent on at least 1 surface of heat ray shielding

resin material described above in any one of the claim numbers from 1 ~ 6.

[Claim 8] The liquid additive used in the manufacture of heat ray shielding resin sheet material has the characteristic of dispersing hexa boride fine particles, or dispersing hexa boride fine particles and ITO fine particles and / or ATO fine particles taken as heat ray shielding component in a transparent resin base material.

[Claim 9] The liquid additive used in the manufacture of heat ray shielding resin sheet material described above in claim number 8 in which the hexa boride mentioned above is at least 1 compound chosen from  $\text{LaB}_6$ ,  $\text{CeB}_6$ ,  $\text{PrB}_6$ ,  $\text{NdB}_6$ ,  $\text{GdB}_6$ ,  $\text{TbB}_6$ ,  $\text{DyB}_6$ ,  $\text{HoB}_6$ ,  $\text{YB}_6$ ,  $\text{SmB}_6$ ,  $\text{EuB}_6$ ,  $\text{ErB}_6$ ,  $\text{TmB}_6$ ,  $\text{YbB}_6$ ,  $\text{LuB}_6$ ,  $\text{SrB}_6$  and  $\text{CaB}_6$ .

[Claim 10] The liquid additive used in the manufacture of heat ray shielding resin sheet material described above in claim number 8 or 9 in which the hexa boride fine particles, ITO fine particles and ATO fine particles have average particle diameter of less than 200 nm.

[Claim 11] The liquid additive used in the manufacture of heat ray shielding resin sheet material described above in any one of the claim numbers from 8 ~ 10 in which the proportion of hexa boride fine particles and ITO fine particles and / or ATO fine particles mentioned above is within the range from 0.1:99.9 ~ 90:10 in terms of weight ratio.

[Detailed description of the invention]

[0001] [Technical field of the invention]

The present invention relates to heat ray shielding resin sheet material that has satisfactory visible light transmittance, excellent heat ray shielding property and excellent impact resistance and water resistance, that is used in roof or walls of buildings, ceiling dome or open part such as window of vehicles.

[0002] [Techniques of the past]

Open part such as window of different buildings or vehicles is being constructed of transparent glass plate or resin plate for allowing sunlight in. However, sunlight contains ultraviolet rays and infrared rays other than visible light rays, particularly, region near infrared rays of 800 ~ 2500 nm of infrared rays is called are heat rays that cause temperature rise in room as they enter from the open part.

[0003] Therefore, use heat ray shielding material controlling the temperature rise in the room simultaneously with retaining the transparency by taking in the visible light rays while shielding the heat rays, as material of windows of buildings and vehicles etc. is being studied and different methods are being proposed for the same.

[0004] For example, heat ray shielding plate obtained by joining heat ray reflective film formed by vapor depositing metal on transparent resin film, to transparent base material such as glass plate, acrylic plate, polycarbonate plate etc. has been presented in Patent number Sho 61 – 277437. However, this heat reflective film itself is extremely expensive and its joining process is extremely complicated and therefore, its cost is extremely high. Moreover, it also had the problem of generating peeling of heat reflective film due to temporal change due to unsatisfactory adhesion between transparent base material and heat reflective film.

[0005] Moreover, many heat ray shielding plates formed by directly vapor depositing

metal or metal oxide on the surface of transparent base material have been proposed, however, vapor deposition device that requires high vacuum or highly accurate controlling of atmosphere has to be used and therefore, its productivity and practicality is bad.

[0006] Moreover, the authors of the present invention proposed heat ray shielding plates obtained by coating the paint used for heat ray shielding containing hexa boride fine particles, or hexa boride fine particles and ITO fine particles and / or ATO fine particles in different binders, and this paint on the surface of transparent base material and then, hardening it, in Patent number Hei 11 – 181336, 2000 – 9603, 2000 – 169765.

[0007] [Problem the invention solves]

As the method of heat ray shielding, the heat ray shielding plate formed by kneading mica covered with titanium oxide taken as heat ray reflective particles, with the transparent resin such as acrylic resin or polycarbonate resin has been proposed in Patent number Hei 5 – 78544 or Hei 2 – 173060, besides the method of forming heat ray shielding reflective film or heat ray shielding film on the transparent base material mentioned above.

[0008] However, in this heat ray shielding plate, large quantity of heat ray reflective particles are required to be added for increasing the heat ray shielding ability and therefore, it has the problem of high addition quantity of heat ray reflective particles and thereby causing lowering of visible ray transmittance. On the other hand, visible ray transmittance increases if addition quantity of heat ray reflective particles is less, however, heat ray shielding property lowers due to which it is difficult to have satisfactory heat ray shielding property and satisfactory visible ray transmittance at the same time. Furthermore, if heat ray reflective particles are blended with large quantity, then properties of transparent resin base material, particularly, impact resistance and rigidity lower.

[0009] In the view of problems mentioned above, the present invention aims at offering a

heat ray shielding material that retains excellent visible light transmittance, shows high heat ray shielding property and has excellent strength such as impact resistance, and that can be manufactured by a simple method without using complicated manufacturing method or expensive physical film formation method.

[0010] [Method to solve the problems]

In order to achieve the aim mentioned above, the authors of the present invention developed the heat ray shielding resin sheet material that has maximum transmittance in the visible light region and minimum transmittance based on showing strong absorption in infrared region based on dispersing hexa boride fine particles having large quantity of free electrons as the component that has heat ray shielding effect in transparent resin such as polycarbonate resin or acrylic resin. Based on this knowledge, the present invention was completed.

[0011] Namely, the heat ray shielding resin sheet material of the present invention has the characteristic of dispersing hexa boride fine particles, or dispersing hexa boride fine particles and ITO fine particles and / or ATO fine particles taken as heat ray shielding component in a transparent resin base material.

[0012] In the heat ray shielding resin sheet material of the present invention mentioned above, the hexa boride mentioned above is at least 1 compound chosen from  $\text{LaB}_6$ ,  $\text{CeB}_6$ ,  $\text{PrB}_6$ ,  $\text{NdB}_6$ ,  $\text{GdB}_6$ ,  $\text{TbB}_6$ ,  $\text{DyB}_6$ ,  $\text{HoB}_6$ ,  $\text{YB}_6$ ,  $\text{SmB}_6$ ,  $\text{EuB}_6$ ,  $\text{ErB}_6$ ,  $\text{TmB}_6$ ,  $\text{YbB}_6$ ,  $\text{LuB}_6$ ,  $\text{SrB}_6$  and  $\text{CaB}_6$ . Moreover, the hexa boride fine particles, ITO fine particles and ATO fine particles are desired to have average particle diameter of less than 200 nm.

[0013] In the heat ray shielding resin sheet material of the present invention mentioned above, the content of heat ray shielding component mentioned above is 0.05 ~ 19 g per 1  $\text{m}^2$  heat ray shielding resin sheet material. The proportion of hexa boride fine particles and ITO fine particles and / or ATO fine particles mentioned above is desired to be within the range from

0.1:99.9 ~ 90:10 in terms of weight ratio. Furthermore, the resin base material mentioned above is desired to be polycarbonate resin or acrylic resin.

[0014] The heat ray shielding resin sheet material forms resin film containing ultraviolet rays absorption agent on at least 1 surface of this heat ray shielding resin material.

[0015] The present invention offers the liquid additive used in the manufacture of heat ray shielding resin sheet material mentioned above. Namely, the liquid additive used in the manufacture of heat ray shielding resin sheet material is the composite used for forming heat ray shielding resin sheet material by mixing with resin or resin raw material and it has the characteristic of dispersing hexa boride fine particles, or dispersing hexa boride fine particles and ITO fine particles and / or ATO fine particles taken as heat ray shielding component in a solvent.

[0016] In the liquid additive used in the manufacture of heat ray shielding resin sheet material of the present invention mentioned above, the hexa boride mentioned above is at least 1 compound chosen from LaB<sub>6</sub>, CeB<sub>6</sub>, PrB<sub>6</sub>, NdB<sub>6</sub>, GdB<sub>6</sub>, TbB<sub>6</sub>, DyB<sub>6</sub>, HoB<sub>6</sub>, YB<sub>6</sub>, SmB<sub>6</sub>, EuB<sub>6</sub>, ErB<sub>6</sub>, TmB<sub>6</sub>, YbB<sub>6</sub>, LuB<sub>6</sub>, SrB<sub>6</sub> and CaB<sub>6</sub>.

[0017] Moreover, in the liquid additive used in the manufacture of heat ray shielding resin sheet material of the present invention mentioned above, the hexa boride fine particles, ITO fine particles and ATO fine particles are desired to have average particle diameter of less than 200 nm. Furthermore, the proportion of hexa boride fine particles and ITO fine particles and / or ATO fine particles mentioned above is within the range from 0.1:99.9 ~ 90:10 in terms of weight ratio.

[0018] [State of practicalization of the invention]

The heat ray shielding resin sheet material of the present invention is obtained by mixing and dispersing hexa boride fine particles, or hexa boride fine particles and ITO fine particles

and / or ATO fine particles taken as heat ray shielding component in a transparent resin base material such as polycarbonate resin or acrylic resin, and it can be formed into any desired shape such as plate, film, spherical surface corresponding to the application.

[0019] The manufacturing method of heat ray shielding resin sheet material can be any desired method as long as fine particles of heat ray shielding component can be homogeneously dispersed in the resin, by the use of it. For example, the method in which the fine particles mentioned above are directly added to resin and these are fusion mixed homogeneously can be used. Particularly, the method in which liquid additive is prepared by dispersing fine particles of heat ray shielding component in a solvent and this liquid additive is formed into resin sheet using the composite mixed with resin or resin raw material, is simple.

[0020] As regards the hexa boride fine particles used as the heat ray shielding component, lanthanum hexa boride ( $\text{LaB}_6$ ), cerium hexa boride ( $\text{CeB}_6$ ), praseodymium hexa boride ( $\text{PrB}_6$ ), neodymium hexa boride ( $\text{NdB}_6$ ), gadolinium hexa boride ( $\text{GdB}_6$ ), terbium hexa boride ( $\text{TbB}_6$ ), dysprosium hexa boride ( $\text{DyB}_6$ ), holmium hexa boride ( $\text{HoB}_6$ ), yttrium hexa boride ( $\text{YB}_6$ ), samarium hexa boride ( $\text{SmB}_6$ ), europium hexa boride ( $\text{EuB}_6$ ), erbium hexa boride ( $\text{ErB}_6$ ), thulium hexa boride ( $\text{TmB}_6$ ), ytterbium hexa boride ( $\text{YbB}_6$ ), lutetium hexa boride ( $\text{LuB}_6$ ), strontium hexa boride ( $\text{SrB}_6$ ) and calcium hexa boride ( $\text{CaB}_6$ ), lanthanum cerium hexa boride ( $(\text{La, Ce})\text{B}_6$ ) etc. can be given.

[0021] Moreover, the used hexa boride fine particles are desired not to undergo oxidation at their surface, however, in most the cases, they do undergo slight oxidation and moreover, oxidation at the surface cannot be avoided in the process of dispersing fine particles and in this case also, its effectiveness of showing heat ray shielding effect does not change. Moreover, higher the completeness of hexa boride fine particles as crystals, higher is the heat ray shielding effect, however, heat ray shielding effect is obtained if basic bond in the internal part of fine

particles is formed from bond between each metal and boron, even if crystallinity is low and broad diffraction peak is obtained in X ray diffraction.

[0022] These hexa boride fine particles can be powder having grayish black color, brownish black color, greenish black color, however, it retains sufficiently high infrared ray shielding property and visible light transmittance in resin sheet in the state of being dispersed in the resin sheet with sufficiently small particle diameter as compared to visible ray wavelength. The reason is not yet clear, however, it is considered that many free electrons are present in these fine particles and therefore, absorbed energy of direct transition between bands by free electrons of internal part of fine particles and that of surface is close to near infrared region from visible light region and therefore, heat rays of this wavelength region are selectively reflected and absorbed.

[0023] Concretely, the resin sheet in which hexa boride fine particles are sufficiently finely and uniformly dispersed, has maximum transmittance between the wavelength 400 nm ~ 700 nm and minimum transmittance between the wavelength 700 nm ~ 1800 nm and furthermore, difference between maximum value and minimum value of transmittance is observed to more than 15 point. It is known that visible light wavelength is between 380 nm ~ 780 nm and it is considered that visibility is bell shaped having peak near 5500 nm and that resin sheet dispersed with hexa boride fine particles effectively transmits visible light and effectively reflects or absorbs other heat rays.

[0024] Moreover, ITO fine particles and ATO fine particles used along with hexa boride fine particles does not absorb or reflect light in visible light region and reflect or absorb in the region of wavelength of more than 1000 nm due to plasma resonance. Moreover, in this transmission profile, transmittance reduces as it inclines towards long wavelength side in near infrared region. On the other hand, in the transmission profile of hexa boride, it has minimum

value near 1000 nm as mentioned above and shows gradual rise in transmittance in long wavelength side. Therefore, heat rays of near infrared region can be shielded and heat ray shielding property improves without reducing visible light transmittance based on using ITO or ATO with hexa boride.

[0025] Average particle diameter of hexa boride fine particles is desired to be less than 200 nm. If average particle diameter is more than 200 nm, then particles undergo coagulation in the dispersion liquid thereby causing sedimentation of fine particles and moreover, it becomes the source of light scattering in the resin and resin sheet appears cloudy. Fine particles of ITO and ATO also are desired to have average particle diameter of less than 200 nm for the reason mentioned above. Moreover, non-transparent light transmittance is required in transparent roof material and in this case, structure supporting the scattering by increasing the particle diameter is desired, however, if particle diameter is rather large, then infrared absorption ability reduces and therefore, average particle diameter is desired to be less than 200 nm.

[0026] Heat ray shielding ability of hexa boride fine particles per unit weight is extremely high and they show similar effect when used with 1/30<sup>th</sup> quantity of ITO or ATO fine particles. Therefore, desired heat ray shielding effect is obtained by using hexa boride fine particles with small quantity and then, in the case of jointly using ITO fine particles or ATO fine particles, quantity of these particles is reduced thereby lowering the cost. Moreover, total usage quantity of all the fine particles can be greatly reduced due to which lowering of properties of resin base material, particularly impact resistance strength and rigidity can be prevented.

[0027] Moreover, absorption of visible light region can be controlled, brightness can be adjusted and privacy can be protected based on controlling the content of hexa boride fine particles or ITO fine particles or ATO fine particles in resin sheet.

[0028] Heat ray shielding ability is decided by the content of heat ray shielding component

per unit surface area of the sheet, however, content of heat ray shielding component with respect to resin is required to be decided depending on the required optical properties and strength of resin sheet material. For example, if resin sheet material is rather thin even if content of heat ray shielding component is such that optical properties are satisfactory, then aberration strength and impact resistance lower. Moreover, there is a possibility of losing the appearance by the floating of heat ray shielding component on the surface of resin sheet material. Therefore, when resin sheet material is thin, concretely thickness is  $20 \sim 30 \mu\text{m}$ , content of heat ray shielding component is desired to be within the range from  $0.05 \sim 19 \text{ g per m}^2$  of resin sheet material. On the other hand, if resin sheet material is thick, then more heat ray shielding component can be contained, however, if thickness of resin sheet material is within the range from  $3 \sim 5 \text{ mm}$ , then visible light transmittance lowers if content of heat ray shielding component is more than  $19 \text{ g / m}^2$ .

[0029] Proportion of hexa boride fine particles and ITO fine particles and / or ATO fine particles when used jointly, should be within the range from 0.1:99.9 ~ 90:10 in terms of weight ratio of hexa boride fine particles : (ITO fine particles and / or ATO fine particles). If hexa boride fine particles are less than this range, then total usage quantity of all the particles cannot be reduced and heat ray shielding property also becomes bad. On the other hand, if hexa boride fine particles are more than this range, then effect of addition of ITO and ATO becomes so small that can be ignored. Moreover, in the case of same optical properties, usage quantity of ITO fine particles and ATO fine particles can be reduced as content of hexa boride fine particles is more and cost reduction can be achieved.

[0030] There is no particular restriction over the method of dispersing heat ray shielding component in resin, as long as fine particles can be dispersed uniformly in the resin. However, the method of using liquid additive obtained by dispersing fine particles in a solvent is desired

to be used. Concretely, liquid additive used in the manufacture of heat ray shielding resin sheet is prepared by dispersing fine particles mentioned above in a solvent by using methods such as beads mill, ball mill, sand mill, ultrasonic waves dispersion etc.

[0031] There is no particular restriction over the dispersion solvent used in the liquid additive used in the manufacture of heat ray shielding resin sheet material and it can be selected considering the resin to be blended and conditions of forming resin sheet material. Organic solvent is generally used. Moreover, pH can be adjusted as per requirement by adding acid or alkali. Furthermore, different surfactants, coupling agents can be added as dispersion agent in order to improve the dispersion stability of fine particles in the resin.

[0032] In order to manufacture heat ray shielding resin sheet material using the liquid additive mentioned above, this liquid additive is added to the resin base material and fine particles are uniformly dispersed in the resin and mixture is prepared by using mixers such as ribbon blender, tumbler, nauta mixer, Henschel mixer, super mixer, planetary mixer etc. or method of fusion mixing by kneaders such as bombarding mixer, kneader, roll, kneader loader, uniaxial extruder, biaxial extruder etc.

[0033] In the case of resin base material being polycarbonate resin, liquid additive is added to bivalent phenol that is the raw material of resin and it is mixed uniformly by well-known methods and it is reacted with carbonate precursor such as phosgene based on which mixture obtained by dispersing fine particles uniformly in resin can be prepared. Moreover, in the case of acrylic resin, liquid additive is added to raw material of acrylic resin such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate etc. and these are uniformly mixed by similar methods and polymerization is carried out by well-known methods such as suspension polymerization or lump polymerization based on which mixture in which fine particles are uniformly dispersed in acrylic resin can be prepared.

[0034] Furthermore, mixture in which fine particles are uniformly dispersed in the resin can be prepared by the method in which the solvent of the liquid additive is removed by common method and the obtained powder is added to the resin and uniform fusion mixing is carried out.

[0035] The resin sheet material of the present invention can be prepared by molding the mixture in which fine particles are uniformly dispersed in the resin mentioned above into flat surface or bent surface material by well-known molding methods such as injection molding, extrusion molding, compression molding etc. Moreover, mixture in which fine particles are uniformly dispersed in the resin can be temporarily pelletized by pulverization device and then resin sheet material can be prepared by the same method. Moreover, thickness of the resin sheet material can be adjusted from thick plate to thin film.

[0036] Heat ray shielding film or ultraviolet rays absorptive film can be formed on the surface of resin sheet material mentioned above. For example, heat ray shielding film can be further formed on the surface by coating the paint obtained by dispersing hexa boride fine particles or ITO fine particles or ATO fine particles in a binder on the resin sheet material. Moreover, ultraviolet rays absorptive film can be formed by coating the paint obtained by dissolving ultraviolet rays absorption agent such as benzotriazole, benzophenone etc. in binder on the resin sheet material mentioned above and then hardening it. Weather resistance of the resin sheet material can be further improved by forming this ultraviolet rays absorptive film.

[0037] Moreover, polycarbonate resin forming the base material of resin sheet material can be obtained by reacting bivalent phenol and carbonate precursor by solution method or fusion method. As regards the bivalent phenol, 2, 2 – bis (4 – hydroxy phenyl) propane [bis phenol A], 1, 1 bis (4 – hydroxy phenyl) cyclo hexane, 2, 2 – bis (4 – hydroxy – 3, 5 – di methyl phenyl) propane, 2, 2 – bis (4 – hydroxy – 3, 5 – di bromo phenyl) propane, 2, 2 – bis (4 – hydroxy – 3

– methyl phenyl) propane, bis (4 – hydroxy phenyl) sulfide, bis (4 – hydroxy phenyl) sulfone etc. can be given. Moreover, bis (4 – hydroxy phenyl) alkanes are desired bivalent phenols and bis phenol A is particularly desired.

[0038] Moreover, as regards the acrylic resin, polymer or copolymer obtained by using methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate as the main raw material and acrylic acid ester possessing alkyl radical having 1 ~ 8 carbon atoms, vinyl acetate, styrene, acrylonitrile, methacrylonitrile etc. as the copolymerization component as per requirement, is used. Moreover, acrylic resin polymerized in multiple steps can also be used.

[0039] Thus, hexa boride fine particles showing strong absorption in near infrared region taken as heat ray shielding component are uniformly dispersed in resin and formed into sheet form based on which heat ray shielding resin sheet material having heat ray shielding functionality and high visible light transmittance can be offered without using expensive physical film formation method or complicated adhesion process.

[0040] Moreover, in the heat ray shielding resin sheet material obtained by dispersing hexa boride fine particles taken as heat ray shielding component in resin along with ATO fine particles and ITO fine particles, heat ray shielding property improves as compared to the case of using these fine particles independently, and moreover, usage quantity of ATO and ITO can be reduced and reduction in cost can be achieved as compared to the case of using only ATO or ITO.

[0041] Furthermore, hexa boride fine particles have low water resistance due to which they have the demerit of getting affected by water thereby changing optical properties. However, resin sheet material is hexa boride fine particles are dispersed of the present invention can shield the contact between hexa boride fine particles and water and change in optical properties can be prevented.

[0042] [Practical examples]

Practical example 1

20 g of LaB<sub>6</sub> fine particles having average particle diameter of 67 nm, 70 g of toluene, water and appropriate quantity of dispersion agent were taken and mixed in ball mill for 100 hours using zirconia ball having diameter of 4 mm and 100 g of liquid additive (A1 liquid) was prepared. Moreover, 20 g of ITO fine particles having average particle diameter of 80 nm, 70 g of toluene, water and appropriate quantity of dispersion agent were taken and mixed similarly in ball mill and 100 g of liquid additive (B1 liquid) was prepared. Furthermore, 20 g of ATO fine particles having average particle diameter of 55 nm, 70 g of toluene, water and appropriate quantity of dispersion agent were taken and mixed similarly in ball mill and 100 g of liquid additive (C1 liquid) was prepared.

[0043] Next, A1 liquid and B1 liquid mentioned above were mixed and additive liquid for polycarbonate was prepared and this liquid additive was added to polycarbonate resin such that concentration of ITO becomes 0.155 weight % and concentration of LaB<sub>6</sub> becomes 0.00097 weight % and fusion mixing was carried out using blender and biaxial extruder after which it was extrusion molded into 3 mm thickness using T die and thus, heat ray shielding polycarbonate sheet material (specimen 1) uniformly dispersed with heat ray shielding fine particles was prepared.

[0044] A1 liquid, polycarbonate resin and B1 liquid and C1 liquid were used and mixed by the method mentioned above with the composition shown as specimen 2 ~ 10 in table 1 and heat ray shielding polycarbonate sheet materials (specimen 2 ~ 10) uniformly dispersed with heat ray shielding fine particles were prepared.

[0045] Spectroscopy properties of each heat ray shielding polycarbonate sheet material of the obtained specimen 1 ~ 10 were measured by using spectrophotometer U-4000 of Hitachi

Seisakujo and visible light transmittance and sunlight transmittance showing heat ray shielding property were calculated as per JISR3106 and the obtained results have been presented in table 1.

[0046] Comparative example 1

B1 liquid and C1 liquid were mixed with polycarbonate resin without using A1 liquid by the similar method as mentioned above with the composition shown as specimen 11 ~ 12 in table 1 and heat ray shielding polycarbonate sheet materials completely uniformly dispersed with ITO or ATO fine particles (specimens 11 ~ 12) were obtained. Same evaluation was carried out on these heat ray shielding polycarbonate sheet materials and results have been presented in table 1.

[0047] Practical example 2

Ultraviolet rays absorptive film was formed on the surface of heat ray shielding polycarbonate sheet material of specimen 2 of practical example 1 mentioned above (joint use of LaB<sub>6</sub> an ITO). Namely, 2 weight % of benzotriazole group ultraviolet rays absorption agent (Chiba Specialty make: product name Chinuvin (?) 384), 10 parts by weight of acrylic resin and 88 parts by weight of toluene were mixed and paint was prepared. 15 g of this paint was coated on the sheet of specimen 2 by a spin coater and heated by putting in an electric furnace of 100°C for 30 minutes and ultraviolet rays absorptive film was formed.

[0048] Evaluation similar to that in practical example 1 was carried out on the obtained heat ray shielding polycarbonate sheet material with ultraviolet rays absorptive film (specimen 13) and results have been presented in table 1.

[0049] Comparative example 2

A1 liquid, C1 liquid and polycarbonate resin were mixed by the similar method as mentioned above with the composition shown as specimen 14 in table 1 and heat ray shielding

polycarbonate sheet material completely uniformly dispersed with heat ray shielding fine particles (specimen 14) was obtained.

[0050] The obtained heat ray shielding polycarbonate sheet material of specimen 14 contained excess quantity of heat ray shielding fine particles due to which floating of heat ray shielding component on the surface was observed and the entire sheet appeared white cloudy. Same evaluation was carried out on these heat ray shielding polycarbonate sheet materials and results have been presented in table 1.

[0051] [Table 1]

Specimen	Heat ray shielding sheet material composition (wt %)			Total fine particles weight (g/m <sup>2</sup> )	Visible light transmittance (%)	Sunlight transmittance (%)
	LaB <sub>6</sub>	ITO	ATO			
1	0.00097	0.155	0	5.79	78	55.6
2	0.0013	0.092	0	3.36	78	54.2
3	0.0018	0.082	0	3.02	78	54.7
4	0.0022	0.067	0	2.49	78	57.5
5	0.0035	0.030	0	1.20	78	59.3
6	0.0050	0	0	0.18	78	59.7
7	0.00097	0	0.51	18.70	78	62.5
8	0.0028	0	0.27	9.82	78	61.3
9	0.0040	0	0.20	7.34	78	61.0
10	0.0042	0	0.15	5.55	78	62.0
11*	0	0.18	0	6.48	78	57.8
12*	0	0	0.61	21.96	78	63.1
13	0.0013	0.092	0	3.36	77	54.2
14*	0.0020	0	0.70	25.27	52	38.1

(Note) Specimen with \* in table are comparative examples.

[0052] It can be understood from the result of table 1 given above that sunlight transmittance can be reduced without lowering visible light transmittance as compared to ITO or ATO of the past based on adding small quantity of LaB<sub>6</sub> as heat ray shielding component.

Moreover, this effect is obtained even if ITO or ATO is not added and in the case of using ITO or ATO jointly, their addition quantity can be greatly reduced.

[0053] For example, in the case of comparing specimen 2 of practical example and specimen 11 of comparative example, in case of sheet material of specimen 2, visible light transmittance was maintained at 78 % and sunlight transmittance lowered to less than 3 points than specimen 11 and addition quantity of ITO could also be reduced to half based on adding 1.39 weight % of LaB<sub>6</sub> of total fine particles in the film.

[0054] Practical example 3

Water resistance experiment was performed on the heat ray shielding polycarbonate sheet material of specimen 4 of practical example 1 mentioned above. Namely, sheet material of specimen 4 was soaked in water for 10 days and then optical properties were once again measured similar to practical example 1 when visible light transmittance was 78 % and sunlight transmittance was 57.5 % and thus, no change in optical properties was observed.

[0055] Practical example 4

20 g of CeB<sub>6</sub> having average particle diameter of 85 nm, 70 g of toluene, water and appropriate quantity of dispersion agent were taken and mixed in ball mill for 100 hours using zirconia ball having diameter of 4 mm and 100 g of liquid additive (D1 liquid) was prepared. D1 liquid, B1 liquid and polycarbonate resin were mixed by similar method as mentioned above with the composition shown as specimen 15 in table 2 and heat ray shielding polycarbonate sheet material completely uniformly dispersed with heat ray shielding fine particles (specimen 15) was obtained.

[0056] Moreover, PrB<sub>6</sub> fine particles, NdB<sub>6</sub> fine particles, GdB<sub>6</sub> fine particles, YB<sub>6</sub> fine particles, SmB<sub>6</sub> fine particles or EuB<sub>6</sub> fine particles were used instead of CeB<sub>6</sub> fine particles mentioned above and liquid additives were similarly prepared. These liquid additives were

mixed with polycarbonate resin and B1 liquid or C1 liquid as per requirement with the composition shown as specimen 16 ~ 21 in table 2 and heat ray shielding polycarbonate sheet materials completely uniformly dispersed with heat ray shielding fine particles (specimen 16 ~ 21) were obtained.

[0057] Same evaluation was carried out on these heat ray shielding polycarbonate sheet materials and results have been presented in table 2.

[0058] [Table 2]

Specimen	Heat ray shielding sheet material composition (wt %)			Total fine particles weight (g/m <sup>2</sup> )	Visible light transmittance (%)	Sunlight transmittance (%)
	6 boride	ITO	ATO			
15	CeB <sub>6</sub> / 0.0020	0.083	0	3.06	77	53.8
16	PrB <sub>6</sub> / 0.0022	0.080	0	2.96	77	54.1
17	NdB <sub>6</sub> / 0.0028	0	0.27	9.82	78	62.1
18	GdB <sub>6</sub> / 0.0027	0	0.29	10.53	78	61.9
19	YB <sub>6</sub> / 0.0018	0.073	0	2.69	78	54.0
20	SmB <sub>6</sub> / 0.0040	0	0.20	7.34	77	61.5
21	EuB <sub>6</sub> / 0.0040	0	0.18	6.62	77	61.8

[0059] It was understood that excellent visible light transmittance and heat ray shielding

effect is obtained even by using hexa boride fine particles such as CeB<sub>6</sub> fine particles, PrB<sub>6</sub> fine particles, NdB<sub>6</sub> fine particles, GdB<sub>6</sub> fine particles, YB<sub>6</sub> fine particles, SmB<sub>6</sub> fine particles and EuB<sub>6</sub> fine particles instead of LaB<sub>6</sub> fine particles as heat ray shielding component.

**[0060] Practical example 5**

20 g of LaB<sub>6</sub> fine particles having average particle diameter of 67 nm, 70 g of toluene, water and appropriate quantity of dispersion agent were taken and mixed in ball mill for 100 hours using zirconia ball having diameter of 4 mm and 100 g of liquid additive (A2 liquid) was prepared. Moreover, 20 g of ITO fine particles having average particle diameter of 80 nm, 70 g of toluene, water and appropriate quantity of dispersion agent were taken and mixed similarly in ball mill and 100 g of liquid additive (B2 liquid) was prepared. Furthermore, 20 g of ATO fine particles having average particle diameter of 55 nm, 70 g of toluene, water and appropriate quantity of dispersion agent were taken and mixed similarly in ball mill and 100 g of liquid additive (C2 liquid) was prepared.

[0061] Next, A2 liquid and B2 liquid mentioned above were mixed and additive liquid for acrylic was prepared and this liquid additive was added to acrylic resin such that concentration of ITO becomes 0.13 weight % and concentration of LaB<sub>6</sub> becomes 0.0012 weight % and fusion mixing was carried out using blender and biaxial extruder after which it was extrusion molded into 3 mm thickness using T die and thus, heat ray shielding acrylic material (specimen 22) completely uniformly dispersed with heat ray shielding fine particles was prepared.

[0062] A2 liquid and acrylic resin and B2 liquid and C1 liquid as per requirement were used and mixed by the method mentioned above with the composition shown as specimen 23 ~ 31 in table 3 and heat ray shielding acrylic materials (specimen 23 ~ 31) uniformly dispersed with heat ray shielding fine particles were prepared.

[0063] Spectroscopy properties of each heat ray shielding acrylic sheet material of the obtained specimen 22 ~ 31 were measured by using spectrophotometer U-4000 of Hitachi Seisakujo and visible light transmittance and sunlight transmittance showing heat ray shielding property were calculated as per JISR3106 and the obtained results have been presented in table 3.

[0064] Comparative example 3

B2 liquid and C2 liquid were mixed with acrylic resin without using A2 liquid by the similar method as mentioned above with the composition shown as specimen 32 ~ 33 in table 3 and heat ray shielding acrylic materials completely uniformly dispersed with heat ray shielding fine particles (specimens 32 ~ 33) were obtained. Same evaluation was carried out on these heat ray shielding acrylic materials and results have been presented in table 3.

[0065] Practical example 6

Liquid additive mixed with A2 liquid and B2 liquid of practical example 5 mentioned above was added to acrylic resin such that concentration of ITO becomes 0.094 weight % and concentration of LaB<sub>6</sub> becomes 0.0012 weight % and fusion mixing was carried out using blender after which it was extrusion molded into 3 mm thickness using T die and thus, heat ray shielding acrylic material completely uniformly dispersed with heat ray shielding fine particles was prepared.

[0066] 2 weight % of benzotriazole group ultraviolet rays absorption agent (Chiba Specialty make: product name Chinuvin (?) 384), 10 parts by weight of acrylic resin and 88 parts by weight of toluene were mixed and this paint was coated on one surface of this heat ray shielding acrylic material by spin coater and heated by putting in an electric furnace of 100°C for 30 minutes and ultraviolet rays absorptive film was formed.

[0067] Evaluation similar to that in practical example 5 was carried out on the obtained heat ray shielding acrylic material with ultraviolet rays absorptive film (specimen 34) and results have been presented in table 3.

[0068] Comparative example 4

A2 liquid, C2 liquid and acrylic resin were mixed by the similar method as mentioned above with the composition shown as specimen 35 in table 3 and heat ray shielding acrylic sheet material completely uniformly dispersed with heat ray shielding fine particles (35) was obtained.

[0069] The obtained heat ray shielding acrylic material of specimen 35 contained excess quantity of heat ray shielding fine particles due to which floating of heat ray shielding component on the surface was observed and the entire sheet appeared white cloudy.

Same evaluation was carried out on these heat ray shielding acrylic materials and results have been presented in table 3.

[0070] [Table 3]

Specimen	Heat ray shielding sheet material composition (wt %)			Total fine particle s weight (g/m <sup>2</sup> )	Visible light transmittance (%)	Sunlight transmittance (%)
	LaB <sub>6</sub>	ITO	ATO			
22	0.0012	0.13	0	4.72	78	55.3
23	0.0016	0.077	0	2.83	78	54.5
24	0.0022	0.068	0	2.53	78	54.9

25	0.0026	0.056	0	2.11	78	56.9
26	0.0042	0.025	0	1.05	78	59.3
27	0.0049	0	0	0.18	78	29.7
28	0.0011	0	0.46	16.60	78	62.9
29	0.0031	0	0.25	9.11	78	62.4
30	0.0044	0	0.18	5.63	78	61.5
31	0.0046	0	0.14	5.20	78	62.9
32*	0	0.18	0	6.48	78	57.3
33*	0	0	0.60	21.60	78	64.9
34	0.0012	0.094	0	3.43	77	55.0
35*	0.0019	0	0.74	26.71	51	37.1

(Note) Specimen with \* in table are comparative examples.

[0071] It can be understood from the result of table 3 given above that sunlight transmittance can be reduced without lowering visible light transmittance as compared to ITO or ATO of the past based on adding small quantity of  $\text{LaB}_6$  as heat ray shielding component. Moreover, this effect is obtained even if ITO or ATO is not added and in the case of using ITO or ATO jointly, their addition quantity can be greatly reduced.

[0072] For example, in the case of comparing specimen 23 of practical example and specimen 32 of comparative example, in case of sheet material of specimen 23, visible light transmittance was maintained at 78 % and sunlight transmittance lowered to less than 3 points than specimen 32 and addition quantity of ITO could also be reduced to half based on adding

2.03 weight % of LaB<sub>6</sub> of total fine particles in the film.

[0073] Practical example 7

Water resistance experiment was performed on the heat ray shielding acrylic material of specimen 25 of practical example 5 mentioned above. Namely, sheet material of specimen 25 was soaked in water for 10 days and then optical properties were once again measured similar to practical example 5 when visible light transmittance was 78 % and sunlight transmittance was 56.9 % and thus, no change in optical properties was observed.

[0074] Practical example 8

20 g of CeB<sub>6</sub> having average particle diameter of 85 nm, 70 g of toluene, water and appropriate quantity of dispersion agent were taken and mixed in ball mill for 100 hours using zirconia ball having diameter of 4 mm and 100 g of liquid additive (D2 liquid) was prepared. D2 liquid, B2 liquid and acrylic resin were mixed by similar method as mentioned above with the composition shown as specimen 36 in table 4 and heat ray shielding acrylic material completely uniformly dispersed with heat ray shielding fine particles (specimen 36) was obtained.

[0075] Moreover, PrB<sub>6</sub> fine particles, NdB<sub>6</sub> fine particles, GdB<sub>6</sub> fine particles, YB<sub>6</sub> fine particles, SmB<sub>6</sub> fine particles or EuB<sub>6</sub> fine particles were used instead of CeB<sub>6</sub> fine particles mentioned above and liquid additives were similarly prepared. These liquid additives were mixed with acrylic resin and B2 liquid or C2 liquid as per requirement with the composition shown as specimen 37 ~ 42 in table 4 and heat ray shielding acrylic materials completely uniformly dispersed with heat ray shielding fine particles (specimen 37 ~ 42) were obtained.

[0076] Same evaluation was carried out on these obtained heat ray shielding acrylic materials 36 ~ 42 and results have been presented in table 4.

[0077] [Table 4]

Specimen	Heat ray shielding sheet material composition (wt %)			Total fine particle s weight (g/m <sup>2</sup> )	Visible light transmittance (%)	Sunlight transmittance (%)
	6 boride	ITO	ATO			
36	CeB <sub>6</sub> / 0.0020	0.085	0	3.13	77	53.3
37	PrB <sub>6</sub> / 0.0022	0.081	0	3.00	77	55.1
38	NdB <sub>6</sub> / 0.0030	0	0.26	9.47	78	63.4
39	GdB <sub>6</sub> / 0.0030	0	0.28	10.19	78	61.9
40	YB <sub>6</sub> / 0.0018	0.073	0	2.69	78	53.7
41	SmB <sub>6</sub> / 0.0039	0	0.21	7.70	77	62.0
42	EuB <sub>6</sub> / 0.0039	0	0.18	6.62	77	62.1

[0078] Practical example 9

Izod impact strength of heat ray shielding polycarbonate sheet material of specimen 10 of practical example 1 mentioned above, heat ray shielding polycarbonate sheet material of specimen 14 having excess content of heat ray shielding component and polycarbonate sheet material not containing heat ray shielding component (specimen 43), was measured as per ASTM D-256. The obtained results have been presented in table 5.

[0079] [Table 5]

Specimen	Total fine particles weight (g/m <sup>2</sup> )	Impact strength (kg·cm·cm <sup>-1</sup> )
10	5.55	77
14*	25.27	35
43*	0	78

(Note) Specimen with \* in table are comparative examples.

[0080] It can be understood that heat ray shielding polycarbonate sheet material of specimen 10 of the present invention has impact resistance similar to polycarbonate sheet material not containing heat ray shielding component of specimen 43. However, in case of the comparative example that is the heat ray shielding polycarbonate sheet material of specimen 14 having excess content of heat ray shielding component, impact strength was remarkably low as compared to specimen 10 and 43 mentioned above.

[0081] [Effect / result of the invention]

The heat ray shielding material that retains excellent visible light transmittance, shows high heat ray shielding property and has excellent strength such as impact resistance, and that can be manufactured by a simple method without using complicated manufacturing method or expensive physical film formation method can be offered by the present invention. Moreover, this heat ray shielding resin sheet material bars direct contact between hexa boride fine particles and water since hexa boride fine particles are dispersed in the resin and therefore, it also has excellent water resistance.

[0082] High heat ray shielding effect is obtained with less content of heat ray shielding component based on the use of hexa boride fine particles that show strong absorption in near infrared region, and their usage quantity reduces in the case of joint use of ATO fine particles or

ITO fine particles and therefore, material cost can be reduced. Furthermore, total fine particles quantity can be greatly reduced due to which lowering of properties of resin base material, particularly lowering of impact resistance strength and rigidity can be prevented.

[0083] Therefore, heat ray shielding resin sheet of the present invention can be used in the open part such as windows of buildings and vehicles and moreover, effect of reducing the cooling load or hot feeling for humans can be obtained since it can bar the sunlight energy coming in from open part and therefore, it is extremely useful for saving energy.

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F Theme (reference)